

MOLECULAR DIFFUSION COEFFICIENTS OF VITAMIN K₃ IN MIXTURES OF CO₂ AND *n*-HEXANE AT TEMPERATURE OF 313.2 K AND TOTAL PRESSURE OF 16.0 MPa

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In this note molecular diffusion coefficients of Vitamin K₃ (2-methyl-1,4-naphthalenedione) in the mixtures of CO₂ and *n*-hexane are measured at a temperature of 313.2 K and a total pressure of 16.0 MPa by the Taylor-Aris tracer response technique^{1,8-10}. The data are then used for finding a correlation of diffusion coefficients of organic substances in multicomponent dense-gas systems.

1. Experiments

The experimental apparatus employed was identical with that used in our previous studies^{2,3}) except for two pumps installed prior to the constant-temperature bath in which a heat exchanger, an injector, a diffusion column and a back-pressure valve were placed. The pump for CO₂ was a Consta Metric Pump III, Milton Roy, U.S.A., and a Hitachi L6000 was employed for *n*-hexane. Vitamin K₃ dissolved in *n*-hexane was injected in the diffusion column (stainless steel tubing of 0.80 ± 0.03 mm I.D. \times 30.86 m; coil diameter of 275 mm), and the response signal was measured with a UV detector (Multi-320 JASCO; at 250 nm) connected to the exit of the column. Vitamin K₃ (purity of 98.5%) purchased from Wako Pure Chemical Ind. was used without further purification. *n*-Hexane was of spectroscopic grade. The mass flow rate of CO₂ was measured with a wet gas meter installed at the very end of the system, and that of *n*-hexane was obtained from the decrease rate of liquid *n*-hexane in a small reservoir attached to the pump. No pressure pulsation was detected in the range of compositions studied. Pressure deviation within 0.1 MPa was observed during the measurements.

2. Results and Discussion

2.1 Diffusion coefficients in mixtures

Figures 1(a) to 1(c) illustrate the apparent diffusion

coefficient data plotted against flow rates of solvent(s). The values of apparent diffusion coefficients, D'_{1i} (where subscript 1 indicates Vitamin K₃, and $i=2, 3$ and m respectively indicate CO₂, *n*-hexane and mixture of CO₂ and *n*-hexane) are found not to depend on u in low-flow rate regions, indicating no effect of secondary flow due to the diffusion column being coiled. Thus the lower-limiting values, represented by the solid lines, are considered to indicate the intrinsic molecular diffusion coefficients, D_{1i} . The value of D_{13} thus obtained is found to agree well with that predicted from the Wilke-Chang equation⁷).

Figure 2 shows the plots of D'_{1m} vs. *n*-hexane mole fraction, x_3 . It was difficult to measure D_{1m} at $x_3 > 0.6$, because in this region no constant and stable flow rate was attained with our apparatus, due to difficulty encountered in the mixing of the two solvents under

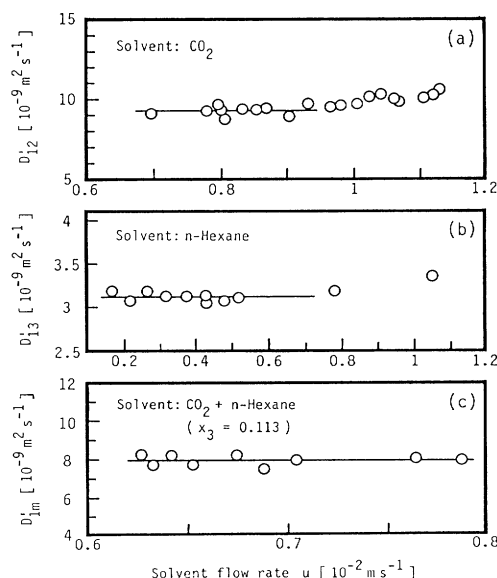


Fig. 1. Apparent diffusion coefficient of Vitamin K₃ vs. flow rate of solvent/mixture of solvents, a: CO₂; b: *n*-hexane; c: CO₂ and *n*-hexane

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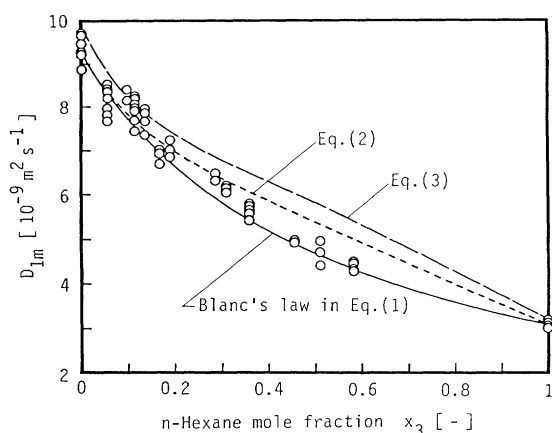


Fig. 2. Diffusion coefficients of Vitamin K₃ measured in the mixture of CO₂ and *n*-hexane at 313.2 K and 16.0 MPa; curves predicted from Eqs (1), (2) and (3)

high pressure. According to the data of Li *et al.*⁵⁾ a single phase is considered to exist at any composition of CO₂ and *n*-hexane within our experimental conditions of 313.2 K and 16.0 MPa.

The temperature of 313.2 K is supercritical for CO₂, but it is subcritical for mixtures of CO₂ and *n*-hexane.

2.2 Prediction of diffusion coefficients in mixtures of CO₂ and *n*-hexane

As far as the authors know, no correlation has been proposed for molecular diffusion coefficients in dense gaseous mixture. Gaseous diffusion coefficients at low pressures may be estimated by Blanc's law⁷⁾:

$$D_{1m} = \frac{1}{\sum_{i \neq 1} (x_i / D_{1i})} \quad (1)$$

For liquid mixtures the following two correlations were proposed by Perkins and Geankoplis⁶⁾:

$$D_{1m} \mu_m^{0.8} = \sum_{i \neq 1} x_i D_{1i} \mu_i^{0.8} \quad (2)$$

$$D_{1m} = 1.9 \times 10^{-18} \frac{(\phi M)^{1/2} T}{\mu_m (V_{b1})^{0.6}} \quad (3)$$

where μ_m is the viscosity of the mixture, and $\phi M = \sum \phi_i x_i M_i$. Note that the physical properties in Eqs. (2) and (3) are in SI units.

The values predicted by Eqs (1), (2) and (3) are also compared in Fig. 2. As depicted, the data in the range of $x_3 \leq 0.2$ agree with Eqs (1) and (2) (although the differences between Eqs (1) and (2) are inappreciable at $x_3 \leq 0.1$); in the range of $x_3 = 0.35-0.6$ the data are well represented by Eq. (1). In general, more accurate prediction may be made by Eqs. (1) and (2) than by Eq. (3), because Eqs. (1) and (2) use the two

binary diffusion coefficient values, respectively, at $x_3 = 0$ and $x_3 = 1$. Note that in the predictions we used the P- ρ -T data of CO₂ reported in the literature⁴⁾, densities of the mixture from Pitzer's correlation⁷⁾, and compressibility factors for simple fluid $Z^{(0)}$ and deviation $Z^{(1)}$ reported by Lee and Kesler⁷⁾. Viscosities of the mixtures were estimated by the method of Chung *et al.*⁷⁾ The viscosity of *n*-hexane at 313.2 K and 16.0 MPa was obtained from the literature¹¹⁾.

In conclusion, molecular diffusion coefficients of Vitamin K₃ measured in mixtures of CO₂ and *n*-hexane at various compositions and at 313.2 K and 16.0 MPa were found to be well predicted by Blanc's law as expressed by Eq. (1).

Nomenclature

D	= molecular diffusion coefficient	[m ² s ⁻¹]
D'	= apparent diffusion coefficient	[m ² s ⁻¹]
M	= molecular weight	[—]
T	= temperature	[K]
u	= flow rate	[m s ⁻¹]
V_b	= molar volume at normal boiling point, estimated by the method of Le Bas quoted in the literature ⁷⁾	[m ³ mol ⁻¹]
x	= mole fraction	[—]
μ	= viscosity	[Pa s]
ϕ	= association factor	[—]

<Subscripts>

c	= critical
m	= mixture of CO ₂ and <i>n</i> -hexane
1	= Vitamin K ₃
2	= CO ₂
3	= <i>n</i> -hexane

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